

# PYROLYSIS AND SOLVOLYSIS OF BIOMASS IN SUPERCRITICAL FLUID SOLVENTS

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## ABSTRACT

The reactions of diaryl ethers and alkanes were examined in water at varying densities. The ethers, namely benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and dibenzyl ether (DBE) underwent parallel pyrolysis and hydrolysis. The former paths led to the usual products described in the literature, whereas the latter led to benzyl alcohol plus phenol, phenethyl alcohol plus phenol and two mols of benzyl alcohol for BPE, PPE and DBE, respectively. 1,2-Diphenylethane (DPE) and 1,3-diphenylpropane (DPP) fragmented according to the neat pyrolysis pathway only, even at the highest water density studied.

The solvolysis was evidently substitution at a saturated carbon atom to which was attached a heteroatom-containing leaving group. Kinetics analysis of the DBE experiments allowed decoupling of the pyrolysis and solvolysis rates, which further permitted correlation of the solvolysis rate constant with the solvent dielectric constant. Good correlation on this Kirkwood plot suggests the solvolysis proceeds through a transition state that is more polar than the reactants.

## INTRODUCTION

The extreme pressure-volume-temperature behavior of fluids at or near their critical point has focussed considerable attention on the extraction of volatiles from, and synfuels-related processing of, high molecular weight, low-volatility materials including biomass [10]. More recently, it has been established that reaction in and with the solvent might assist [1, 7, 15]. However, information about the kinetics and mechanisms controlling these reactions is usually obscured during experiments with actual biomass by the complexity of the substrate and its structure. This motivates the use of model compounds whose structures and product spectra are well enough characterized to allow the deduction of reaction pathways, kinetics and mechanisms.

The present report is of a probe into the effect of supercritical water on the reaction paths of the

diaryl ethers BPE, PPE and DBE and the diaryl alkanes DPE and DPP. The thermal reactions of these compounds having been well studied previously, they afforded an excellent opportunity to explore the effect of supercritical water on their reactions.

## EXPERIMENTAL

The model compounds were reacted neat and in water at conditions summarized in Table 1. The reduced density of water ( $\rho_{r,w} = \rho/\rho_{c,w}$ ) ranged from 0.0 to 2.1. Except for PPE, the reactants, solvents, and GC standards were commercially available and used as received. PPE was synthesized according to the method of Mamedov and Khydyrov [8].

A typical experimental procedure was as follows: measured amounts of the reactant, solvent and the demonstrably inert [15] internal standard biphenyl were loaded into "tubing-bomb" reactors comprising one 1/4 in. stainless steel Swagelok port connector and two end caps. These constant volume batch reactors had a volume of 0.59 cm<sup>3</sup>. Sealed reactors were immersed into a fluidized sand bath and reached the desired reaction temperature,  $\pm 2^\circ\text{C}$ , in about 2 minutes. After the desired time had passed, the reactions were quenched by immersion in a cold water bath.

Reaction products were collected as a single phase in acetone. Subsequent product identification was by GC-MS; and routine quantitation was by gas chromatography on an HP 5880 instrument equipped with a 50 M SE-54 or DB-5 fused silica capillary column and flame ionization detector. Response factors were estimated by analysis of standard mixtures.

## RESULTS

Experimental results are presented in sections allotted to each model compound. Within each section, results are presented in terms of reaction products and kinetics, first for pyrolysis and then for reaction in water.

**Benzyl Phenyl Ether.** Neat pyrolysis of benzyl phenyl ether (BPE) at 332°C led to phenol and toluene as stable primary products, as indicated by their positive initial and zero final slopes in Figure 1, a plot of molar yield ( $n_i/n_{1,0}$ ) vs. reaction time. Minor products included, in order of decreasing yield, o-hydroxydiphenylmethane (OHD), p-hydroxydiphenylmethane (PHD), diphenylmethane, benzaldehyde, benzene, 1,2-diphenylethane and t-stilbene. Linear regression showed the apparent first-order disappearance rate constant for BPE at 332°C to be  $9.45 \times 10^{-4} \text{ s}^{-1}$ .

BPE reaction in water, at 332°C and an overall water loading  $\rho_{r,w} = 1.6$ , was almost four times as fast as neat pyrolysis at the same reaction temperature. Figure 1 also illustrates the differences

between the product spectra for neat pyrolysis of BPE and its reaction in water at  $\rho_{r,w}=1.6$ . Benzyl alcohol, produced in only trace quantities during neat pyrolysis, was a major hydrolysis product. After reaching its maximum yield of 0.45 at 8 minutes, benzyl alcohol underwent secondary reaction to extinction by 45 minutes.

The ultimate yields of the stable products OHD and PHD were also dependent upon  $\rho_{r,w}$ . The maximum OHD yield of 0.098 observed during neat pyrolysis at 332° C was about one third of the value of 0.26 observed from reaction in water at  $\rho_{r,w}=1.6$ . Similarly the yield of PHD increased from a value of 0.05 after 45 minutes during neat pyrolysis to a value of 0.18, after only 30 minutes, during reaction of BPE in water.

The effect of  $\rho_{r,w}$  on reaction of BPE in water is illustrated in Figure 2 as a plot of product selectivity ( $s_i=y_i/x$ ) vs.  $\rho_{r,w}$  for a constant reaction time of 5.6 minutes. BPE conversion ( $x$ ) increased monotonically with reduced water density from a value of 0.85 at  $\rho_{r,w}=0.0$  to essentially unity for  $\rho_{r,w} \geq 1.5$ . Selectivity to the pyrolysis product toluene decreased with increasing water density from 0.25 at  $\rho_{r,w}=0.0$  to 0.05 at  $\rho_{r,w}=2.1$ . Selectivity to phenol, which resulted from both pyrolysis and solvolysis, increased from a low value of 0.58 at  $\rho_{r,w}=0.0$  to 0.80 at  $\rho_{r,w} \geq 1.1$ . Selectivity to benzyl alcohol increased from 0.0 at  $\rho_{r,w}=0.0$  to a maximum of about 0.50 at  $\rho_{r,w}=1.2$ , at which point secondary reactions of benzyl alcohol were significant by 5.6 minutes. Furthermore, but not illustrated in Figure 2, the selectivity to both OHD and PHD increased, as  $\rho_{r,w}$  increased from 0.0 to 2.1, from lows of 0.08 and 0.03 to highs of 0.21 and 0.13 for OHD and PHD, respectively.

These results suggest that reaction of BPE in water is a combination of a thermal pathway leading to phenol and toluene and a hydrolysis pathway that yields phenol and benzyl alcohol. The thermal pathway is like that reported for BPE thermolysis by Brüker and Kölling [2], Schlosberg et al. [13], Sato and Yamakawa [11] and Kamiya et al. [5]. The hydrolysis reaction is the addition of one mol of water to one mol of BPE producing one mol each of phenol and benzyl alcohol. Selectivity to the hydrolysis pathway increased with increases in reduced water density.

**Phenethyl Phenyl Ether.** The major primary products from the neat pyrolysis of phenethyl phenyl ether (PPE) were phenol and styrene. Styrene underwent secondary decomposition to ethyl benzene, toluene, benzene and other minor products. PPE reaction in water also led to phenol and styrene, but in addition afforded phenethyl alcohol. Reactions in  $H_2^{18}O$  showed incorporation of the label into the phenethyl alcohol.

The influence of  $\rho_{r,w}$  on the selectivity to products at 413° C is summarized in Figure 3 as a plot of  $s_i$  vs.  $\rho_{r,w}$  for a constant reaction time of 16 minutes. PPE conversion was about 0.40 at  $\rho_{r,w}=0.0$  and leveled off at 0.25 for  $\rho_{r,w}\geq 0.2$ . Selectivity to styrene increased from 0.29 at  $\rho_{r,w}=0.0$  to an average value of 0.52 for  $\rho_{r,w}\geq 0.2$ . Selectivity to phenol averaged at about 1.0. The selectivity to phenethyl alcohol increased from essentially zero at  $\rho_{r,w}=0.0$  to 0.06 at  $\rho_{r,w}=1.4$ .

These results suggest that the overall reaction of PPE in water is by two paths, the first of which being pyrolysis to phenol and styrene and the second of which being hydrolysis to phenol and phenethyl alcohol. The neat pyrolysis pathway is identical to that observed by Klein and Virk [6]. The hydrolysis of PPE was equivalent to the addition of one mol of water to one mol of PPE to produce one mol each of phenol and phenethyl alcohol.

**Dibenzyl Ether.** Neat pyrolysis of dibenzyl ether (DBE) at 374° C led to toluene and benzaldehyde as major primary products. Its reaction in water at 374° C led to benzyl alcohol, toluene, benzaldehyde, and oligomers. DBE decomposition in water at  $\rho_{r,w}=1.6$  was about 3.5 times as fast as neat pyrolysis; benzyl alcohol was the major and essentially the only primary product at this water density. The yield of benzyl alcohol reached a maximum and then decreased at longer times as it reacted to oligomers. The foregoing suggests that DBE reaction in water comprises two parallel pathways, with the first being identical to the neat pyrolysis reported by Schlosberg et al. [12] and also thermolyses in hydrogen donor noted by Brücker and Kölling [2], Cronauer et al. [3] and Simmons and Klein [14]. The second pathway is hydrolysis of one DBE mol to two benzyl alcohol mols.

**1,2-Diphenylethane.** Neat pyrolysis of 1,2-diphenylethane (DPE) at 500° C produced toluene as the major and primary product; t-stilbene, benzene, ethyl benzene, phenanthrene, and diphenylmethane were all minor primary products. Trace amounts of styrene and triphenylethylene were also present.

Reaction of DPE in water at 500° C and  $\rho_{r,w}=1.4$  also led to toluene as the major primary product. Observed minor products were those formed during neat pyrolysis. Products' yields from neat pyrolysis and reaction in water were virtually identical. Thus, no additional pathways were identified for the reaction of DPE in water.

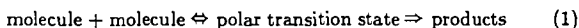
**1,3-Diphenylpropane.** Neat pyrolysis of 1,3-diphenylpropane (DPP) at 420° C led to toluene and styrene; styrene underwent secondary conversion to other products including ethyl benzene.

Minor products included 1,2-diphenylethane, benzene, and n-propyl benzene, all present in molar yields of less than 0.05. Reaction of DPP in water at 420° C and  $\rho_{r,w}=1.6$  led to the same products in approximately the same molar yields as did pyrolysis. Thus pyrolysis was the lone operative pathway during reaction of DPP in water.

## DISCUSSION

Reaction of the diaryl ethers BPE, PPE and DBE in water was via parallel pyrolysis and solvolysis pathways. The diaryl alkanes DPE and DPP, on the other hand, fragmented by only a neat pyrolysis pathway, even at the largest  $\rho_{r,w}$  studied. Since all of the model compounds pyrolyse by a set of free-radical elementary steps, it is reasonable to suspect that solvolysis does not proceed through a transition state involving water and a thermally generated radical. In fact, the empirical observation that solvolysis occurred between water and an organic molecule with a saturated carbon to which was attached a heteroatom-containing leaving group suggests the chemistry may be like the classic liquid-phase nucleophilic substitution at saturated carbon. Solvolysis involving supercritical methanol and also a N- containing organic has been observed also [1]. Note that heterocyclics, devoid of saturated carbons, did not undergo solvolysis. Another mechanism must therefore govern the solvolysis reaction.

Thus the transition state is likely more polar than the reactants, which are neutral molecules. The class of reaction illustrated in Equation (1)



is amenable to division of the free energy of activation  $\Delta G^\ddagger$  into an electrostatic and a non-electrostatic part, the former being influenced by the solvent dielectric constant as developed in the classic Kirkwood analysis. For the present reactions, where the activated complex is more polar than the reactants, the solvolysis rate constant should increase with increasing solvent dielectric constant [9] and afford a linear correlation of  $\ln k_s$  with the function  $(\epsilon-1/\epsilon)$ .

The kinetics data for reaction of DBE in water at 374° C were reduced for pyrolysis and solvolysis rate constants for each  $\rho_{r,w}$  studied. The solvolysis rate constant and Franck's [4] measurements of  $\epsilon$  vs.  $\rho$  for water allowed construction of the Kirkwood plot of Figure 4. The linear relationship between  $\ln k_s$  and  $\rho_{r,w}$  supports the proposed polar transition state.

## SUMMARY AND CONCLUSIONS

1. Reaction in water of the diaryl ethers was by parallel pyrolysis and solvolysis. The diaryl alkanes afforded only pyrolysis products, even at reduced water densities of greater than 1.4.
2. Whereas the pyrolysis occurred via a set of free-radical elementary steps, the solvolysis was likely via nucleophilic substitution that proceeded through a polar transition state.

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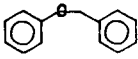
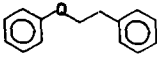
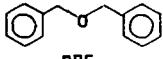
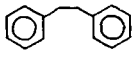
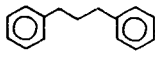
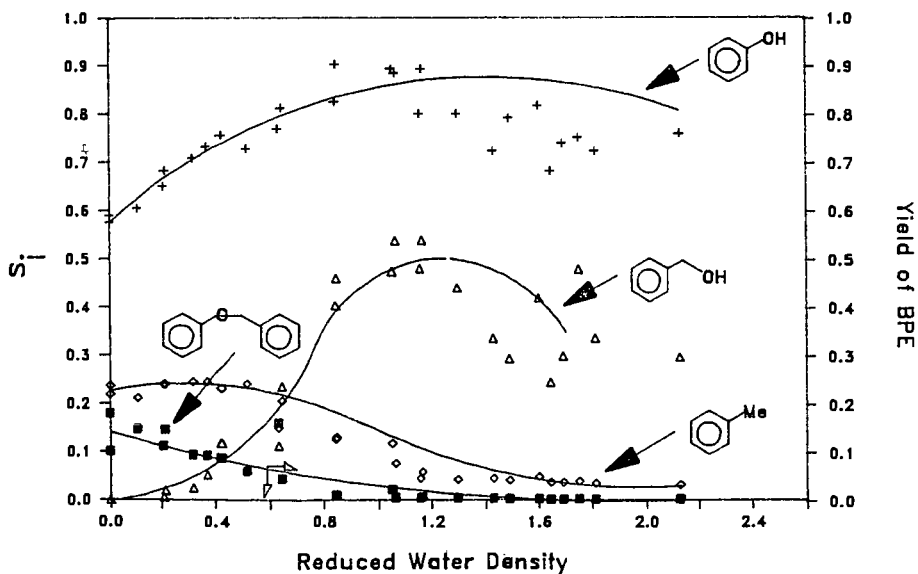
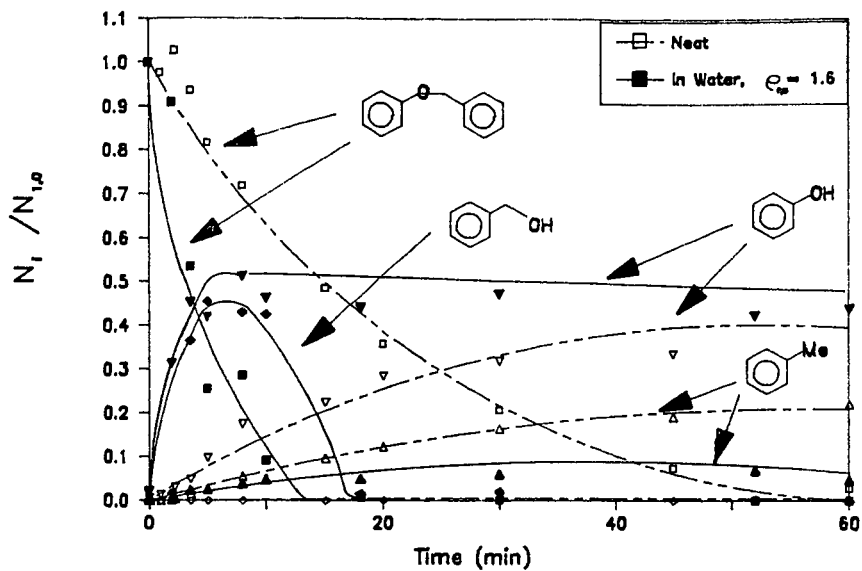
Reactant	T(°C)	$\phi_{r,w}$	t (min)
 BPE	332 377	0, 1.6 0.0-2.1	0-60 5.6
 PPE	413	0.0-1.4	16
 DBE	374	0.0-1.6	0-60
 DPE	500	0.0, 1.4	0-180
 DPP	420	0.0, 1.6	0-60

Table 1: Summary of Experimental Conditions



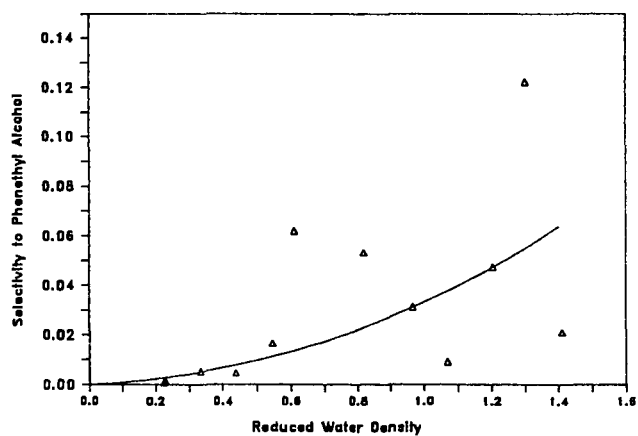
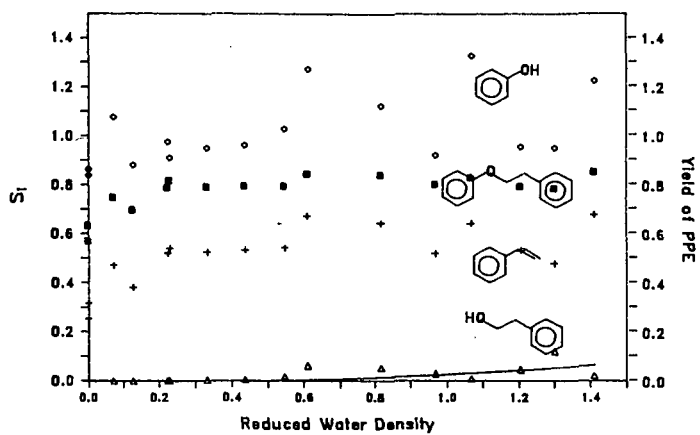
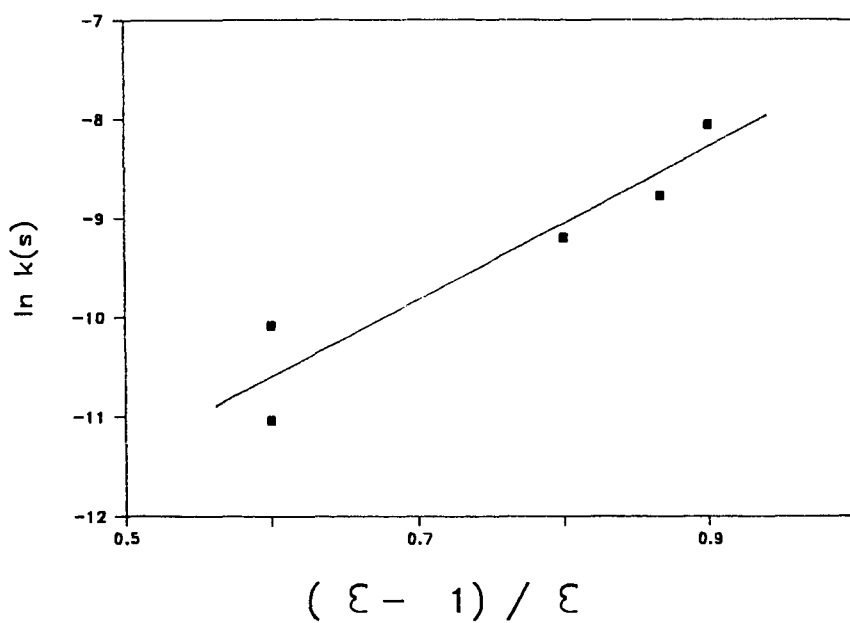


Figure 3: Reaction of Phenethyl Phenyl Ether in Water  
 $T = 413^{\circ}\text{C}$ ,  $t = 16$  minutes



**Figure 4:** Variation of  $k_s$  with Solvent Dielectric Constant  
Reaction of DBE in Water,  $T = 374^\circ \text{C}$